

# EXAMPLES for Tramonto: A Density Functional Theory code for inhomogeneous fluids at equilibrium or steady state

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# 1 Introduction

This document details a suite of test problems that accompanies the Tramonto code. This test suite is found in a directory Tramonto/Examples. Here we briefly discuss each of the test problems, present some input files and density distributions, and give the principle outputs (adsorptions, free energies, and forces, etc.) for each case. This test suite should be used to test any new additions to the code, and examples of new capabilities should be added to the test suite as they become available. Note that under Tramonto/Examples, the input files are found in the directories Ex\_inputs, Ex\_surfaces, Ex\_crfles, Ex\_polyfiles, and Ex\_restarts. The density profile outputs for each case are found in the directory Ex\_dens\_outputs. If a case fails, using the old density output with a restart may be helpful in locating new bugs.

## 2 1D Atomic Fluids at Equilibrium

### 2.1 1 Component Neutral, Hard Sphere system

#### 2.1.1 Case 1Dhn1: Two confining surfaces, high resolution

This case solves for a one-component hard sphere fluid confined by two hard walls at high resolution.

#### 2.1.2 Case 1Dhn2: 2 confining surfaces, lower resolution

This case repeats case 1 at a lower resolution.  $Esize_x[0] = 0.1$ . Principle output for cases 2-11 are given in the table below.

#### 2.1.3 Case 1Dhn3: 2 confining surfaces, reflective boundary

This case repeats case 2, but in a domain with a reflective boundary on the right side and a total domain size of  $3\sigma$ .

#### 2.1.4 Case 1Dhn4: 2 confining surfaces, opposite reflective boundary

This case is identical to case 3, but exchanges the left and right boundaries.

#### 2.1.5 Case 1Dhn5: 1 surface, bulk boundary condition, Matrix\_fill\_flag=0

This case is a  $10\sigma$  domain with a wall at the left side and a bulk fluid at the right side. It has Matrix\_fill\_flag=0.

#### 2.1.6 Case 1Dhn6: 1 surface, Matrix\_fill\_flag=1

Same as Case 5 with Matrix\_fill\_flag=1.

#### 2.1.7 Case 1Dhn7: 1 surface, Matrix\_fill\_flag=2

Same as Case 5 with Matrix\_fill\_flag=2.

#### 2.1.8 Case 1Dhn8: 1 surface, Matrix\_fill\_flag=3

Same as Case 5 with Matrix\_fill\_flag=3.

#### 2.1.9 Case 1Dhn9: 1 surface, Matrix\_fill\_flag=4

Same as Case 5 with Matrix\_fill\_flag=4.

#### 2.1.10 Case 1Dhn10: 1 surface, bulk boundary, 4 zones

Same as Case 5 with the domain split into 4 zones with the break points at  $2\sigma$ ,  $4\sigma$ , and  $6\sigma$  from the surface.

### 2.1.11 Case 1Dhn11: 1 surface, 4 zones, Coarser Jacobian

Same as Case 10 with the Jacobian integrals always based on a mesh of  $0.2\sigma$ .

Case	niter	Ex. Ads	Total Ads	Surf. Free Energy	Force
1Dhn1	5	-0.222308	3.527692	2.287919	5.231941867
1Dhn2	5	-0.224384	3.525616	2.393064	5.022083086
1Dhn3	5	-0.224384	3.525616	2.393064	5.022083086
1Dhn4	5	-0.224384	3.525616	2.393064	5.022083086
1Dhn5	5	-0.116036	7.008964	1.198788	4.956897154
1Dhn6	11	-0.116045	7.008955	1.198789	4.956749333
1Dhn7	11	-0.116046	7.008954	1.198787	4.956747236
1Dhn8	5	-0.116036	7.008964	1.198788	4.956897154
1Dhn9	11	-0.116043	7.008957	1.198787	4.956819690
1Dhn10	5	-0.115843	7.009157	1.149949	5.164672453
1Dhn11	5	-0.115843	7.009157	1.149949	5.164672453

Table 1: Principle output for 1-dimensional hard sphere/ hard wall cases in the test suite.

## 2.2 1 Component Neutral Lennard-Jones Fluids

### 2.2.1 Case 1Dljn1: LJ Fluid near LJ wall

Dense LJ fluid near a 9-3 LJ wall. (Check the active potential in the dft\_potentials.c file if incorrect answers are obtained. Those given here were generated with the cut and shifted 9-3 potential.

### 2.2.2 Case1Dljn2: Test mixing rule

Same as Case 12, but with manual input of wall-fluid parameters.

### 2.2.3 Case 1Dljn3: Test long wall-fluid cutoffs

Same as Case 12, but with wall-fluid cutoff increased from 3 to 20.

### 2.2.4 Case 1Dljn4: Test LJ12-6 integrated walls

Same as Case 14, but does explicit integration of 12-6 potential for external field. Note that the force calculation is not working for this case yet.

Case	niter	Ex. Ads	Total Ads	Surf. Free Energy	Force
1Dljn1	6	-0.178167	6.946833	-2.861495	1.625346852
1Dljn2	6	-0.178167	6.946833	-2.861495	1.625346852
1Dljn3	6	-0.134113	6.990887	-3.578393	1.635907510
1Dljn4	6	-0.137941	6.987059	-3.527798	0.000000000

Table 2: Principle output for 1-dimensional hard sphere/ hard wall cases in the test suite.

## 2.3 Mixtures

### 2.3.1 Case 1Dmix1: 2 components - neutral hard spheres

Two component neutral hard sphere system with same total density as case all of the above cases. Compare results to case 6 above.

### 2.3.2 Case 1Dmix2: 2 components - neutral Lennard-Jones fluid

Two component neutral Lennard-Jones system with same total density as case all of the above cases. Compare results to case 14 above.

### 2.3.3 Case 1Dmix3: 2 components - Poisson-Boltzmann fluid

Two component Poisson-Boltzmann fluid with surface charge density of 0.3, and total ion density of 0.1 in a 1-1 electrolyte. Note that the free energy computation for this system is not correct at this point.

### 2.3.4 Case 1Dmix4: 2 components - Primitive Model fluid

Two component 1-1 electrolyte of total density 0.1. Finite sized particles of equal size. Two confining surface each with a surface charge density of 0.3. Note that the free energy computation for this system is not correct at this point.

### 2.3.5 Case 1Dmix5: 2 components - Primitive Model fluid - with $c(r)$ corrections

Same as case 1Dmix4, but with corrections to the direct correlation function.

### 2.3.6 Case 1Dmix6: 3 components - Civilized Model fluid

Same as case 1Dmix4, but also treats the solvent as a finite sized particle. The bulk solvent density is set to 0.65.

### 2.3.7 Case 1Dmix7: 3 components - LJ electrolyte

Same as 1Dmix6, but with LJ terms also turned on. The external field has the coulomb contribution and a 9-3 LJ interaction. The wall-fluid interaction energy is 3. All cutoffs are set to  $3\sigma$ .

### 2.3.8 Case 1Dmix8: 3 components - LJ electrolyte # 2

Same as 1Dmix7, but with a coarse mesh.

### 2.3.9 Case 1Dmix9: 3 components - LJ electrolyte # 3

Same as 1Dmix8, but with a smaller domain and a reflective boundary on the right side.

Case	niter	Ex. Ads[0]	Ex. Ads[1]	Ex. Ads[2]	Surf. Free Energy	Force
1Dmix1	5	-0.058018	-0.058018	N/A	1.198788	4.956897154
1Dmix2	11	-0.067056	-0.067056	N/A	-3.578393	1.635907510
1Dmix3	8	-0.107513	0.492487	N/A	N/A	N/A
1Dmix4	8	-0.185832	0.414168	N/A	N/A	N/A
1Dmix5	8	-0.160379	0.439621	N/A	N/A	N/A
1Dmix6	8	-0.149902	0.450098	-0.502953	N/A	N/A
1Dmix7	13	-0.165082	0.434918	-0.607667	N/A	N/A
1Dmix8	8	-0.164617	0.435383	-0.674387	N/A	N/A
1Dmix9	7	-0.160178	0.439822	-0.666253	N/A	N/A

Table 3: Principle output for 1-dimensional mixture cases in the test suite.

## 3 1D Polymer Fluids at Equilibrium

### 3.1 Case 1Dpoly1: 8-2-8 repulsive polymer at a hard wall

Total polymer density in the bulk is 0.711. This case does not require a restart from a file. For polymer cases always check the stoichiometry. For the 8-2-8 case, the adsorption of the tail beads should be 16/18 of the total and the adsorption of the head beads should be 2/18 of the total.

### 3.2 Case 1Dpoly2: 8-2-8 attractive polymer at an attractive wall

In this case, the familiar 9-3 LJ potential is used in the dft\_potentials.c file.

### 3.3 Case 1Dpoly3: 8-2-8 polymer in a single site solvent

This system forms a model lipid bilayer. Again an intelligent initial guess is needed for convergence.

### 3.4 Case 1Dpoly4: Charged 8-2-8 polymer in a single site solvent

The tail (8) segments of the polymer carry a charge of -0.0125 while the head (2) segments of the polymer carry a charge of 0.1. The profile from case 26 is used as the initial guess with the electrostatic field set to 1 everywhere in the domain. This case demonstrates charged polymers and tests the Restart=3 option where the densities, fields, and propagator equations are taken from the files and PDE quantites (electrostatic field, chemical potential fields) are set to something simple.

### 3.5 Case 1Dpoly5: Type\_poly=1

This case is the same as case 1Dpoly4 except option Type\_poly=1 is chosen to solve the system of equation. Again, the same input density from 1Dpoly3 is used with Restart=3.

### 3.6 Case 1Dpoly6: Type\_poly=2

This case is the same as case 1Dpoly4 except option Type\_poly=2 is chosen to solve the system of equation. Again, the same input density from 1Dpoly3 is used with Restart=3.

Case	niter	Ads[0]	Ads[1]	Ads[2]	Surf. Free Energy
1Dpoly1	9	19.611163	2.362834	N/A	-5.536430
1Dpoly2	10	19.335234	2.416904	N/A	-4.355118
1Dpoly3	1	3.525591	0.440699	27.666943	-26.314286
1Dpoly4	4	3.489204	0.436150	27.700606	-26.254234
1Dpoly5	4	3.489204	0.436150	27.700606	-26.254234
1Dpoly6	3	3.489204	0.436150	27.700606	-26.254234

Table 4: Principle output for 1-dimensional polymer cases in the test suite.

## 4 2D/3D Atomic Fluids Tests

### 4.1 Case 2D3Datomic1: LJ Electrolyte in 2D - y reflections

This case is identical to 1Dmix8 except it is solved in a 2D domain with reflective boundary conditions in y.

### 4.2 Case 2D3Datomic2: LJ Electrolyte in 2D - x reflections

This case is identical to 2D3Datomic1 except the surface normals are rotated 90°, and the reflective boundary conditions are in the x-direction.

#### **4.3 Case 2D3Datomic3: LJ Electrolyte in 2D - y periodic**

This case is identical to 2D3Datomic1, but has periodic boundary conditions in y.

#### **4.4 Case 2D3Datomic4: LJ Electrolyte in 2D - x periodic**

This case is identical to 2D3Datomic2, but has periodic boundary conditions in x.

#### **4.5 Case 2D3Datomic5: LJ Electrolyte in 2D - x continuation**

This case is identical to 2D3Datomic1, but has periodic boundary conditions in x.

#### **4.6 Case 2D3Datomic6: LJ Electrolyte in 2D - y continuation**

This case is identical to 2D3Datomic2, but has periodic boundary conditions in y.

#### **4.7 Case 2D3Datomic7: LJ Electrolyte in 3D - y and z reflections**

This case is identical to 1Dmix9 except (1) it is solved in a 3D domain with reflective boundary conditions in both y and z, and (2) the size of the domain in x is halved with a reflective boundary on the right side.

#### **4.8 Case 2D3Datomic8: LJ Electrolyte in 3D - x and z reflections**

This case is identical to 2D3Datomic7 except it is solved in a 3D domain with reflective boundary conditions in both x and z.

#### **4.9 Case 2D3Datomic9: LJ Electrolyte in 3D - x and y reflections**

This case is identical to 2D3Datomic7 except it is solved in a 3D domain with reflective boundary conditions in both x and y.

#### **4.10 Case 2D3Datomic10: LJ Electrolyte in 3D - y and z periodic**

This case is identical to 2D3Datomic7 except there are now periodic boundaries in y and z.

#### **4.11 Case 2D3Datomic11: LJ Electrolyte in 3D - y and z continue**

This case is identical to 2D3Datomic7 except there are now reflective boundaries in y and z.

#### **4.12 Case 2D3Datomic12: LJ Electrolyte in 3D - y continue and z periodic**

This case is identical to 2D3Datomic7 except there are continuation boundaries in y and periodic boundaries z.

### **5 Continuation Tests**

#### **5.1 Case 1Dcont1:**

0th order continuation varying all densities simultaneously. 1 component Lennard-Jones fluid. Set to compute 30 steps, actually generates 22 solutions. Data for the first, tenth and last are shown below.

#### **5.2 Case 1Dcont2:**

Arc-length continuation, but otherwise identical to the 1Dcont1 case. Again set up to compute 30 steps. Actually computes 29 solutions. Data for the first, tenth, and last are shown below.

Case	niter	Ex_Ads[0]	Ex_Ads[1]	Ex_Ads[2]	Surf. Free Energy
2D3Datomic1	9	-0.164613	0.435387	-0.674180	N/A
2D3Datomic2	9	-0.164613	0.435387	-0.674180	N/A
2D3Datomic3	11	-0.164613	0.435387	-0.674180	N/A
2D3Datomic4	11	-0.164613	0.435387	-0.674180	N/A
2D3Datomic5	10	-0.164613	0.435387	-0.674180	N/A
2D3Datomic6	10	-0.164613	0.435387	-0.674180	N/A
2D3Datomic7	10	-0.160170	-0.439830	-0.666005	N/A
2D3Datomic8	10	-0.160170	-0.439830	-0.666005	N/A
2D3Datomic9	10	-0.160170	-0.439830	-0.666005	N/A
2D3Datomic10	11	-0.160170	-0.439830	-0.666005	N/A
2D3Datomic11	10	-0.160170	-0.439830	-0.666005	N/A
2D3Datomic12	10	-0.160170	-0.439830	-0.666005	N/A

Table 5: Principle output for 2 and 3-dimensional problems to test various boundary conditions.

### 5.3 Case 1Dcont3:

Tests spinodal tracking algorithms. Finds the spinodal point in the temperature-density plane. Set up to compute 14 steps. Actually computes 12 solutions. Data for the first, fifth, and last are shown below.

### 5.4 Case 1Dcont4:

Tests binodal tracking algorithms. Tracks a binodal in the temperature-density plane. Set up to compute 10 steps. Actually computes 11 solutions. Data for the first and last are shown in the table.

Case	niter	$kT/\epsilon_{ff}$	$\rho_b$	Ex_Ads[0]	force	Surf. Free Energy
1Dcont1 (1)	9	0.769230769	0.00000100	0.000415	0.000001489	-0.000422
1Dcont1 (10)	4	0.769230769	0.00124611	1.314452	0.001821120	-1.504508
1Dcont1 (22)	4	0.769230769	0.00506460	2.915346	-0.106074043	-3.943196
1Dcont2 (1)	9	0.769230769	0.00000100	0.000415	0.000001489	-0.000422
1Dcont2 (10)	3	0.769230769	0.00044223	0.848369	0.000653671	-0.344495
1Dcont2 (29)	3	0.769230769	0.00677950	4.681015	-0.319105662	-0.5916833
1Dcont3 (1)	9	0.769230769	0.00506755	2.933112	-0.115707404	-3.944801
1Dcont3 (5)	3	0.8892308	0.01242808	2.638086	-0.091864069	-3.278197
1Dcont3 (12)	4	1.0729808	0.03475432	2.456827	-0.086154772	-2.753229
1Dcont4 (1A)	9	0.769230769	0.00345787	2.021229	0.003030797	-3.036407
1Dcont4 (1B)	9	0.769230769	0.00345787	4.391266	-0.94904113	-3.036407
1Dcont4 (11A)	9	1.0692308	0.03405399	2.373717	-0.065367901	-2.756242
1Dcont4 (11B)	9	1.0692308	0.03405399	2.640730	-0.131511943	-2.756242

Table 6: Principle output for test cases centered on continuation algorithms.